

Annual Scientific Report

on

FUNDAMENTAL PROCESSES IN PARTIALLY IONIZED PLASMAS

Grant AFOSR-88-0264

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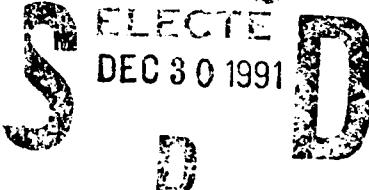


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Submitted by

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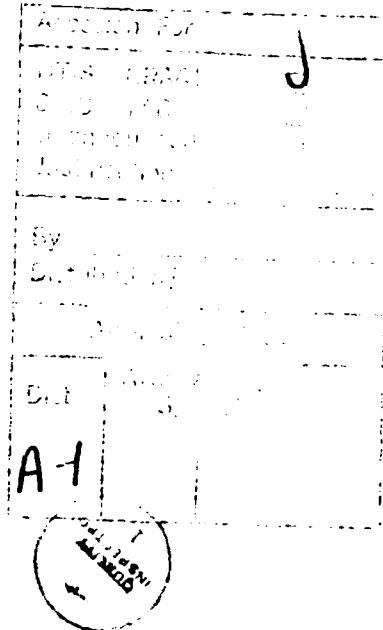
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1.0 INTRODUCTION

This report describes progress on a research program on the fundamental processes in partially ionized plasmas conducted in the High Temperature Gasdynamics Laboratory at Stanford University. This research is supported by a grant from the Air Force Office of Scientific Research (AFOSR-88-0264) and is currently conducted under the direction of Professor Charles H. Kruger. Two Ph.D. candidates are currently finishing their doctoral research and three students have completed their Ph.D. under this program. These three currently have faculty positions at other universities. Another student has also accepted a faculty position.

Several space power and propulsion systems of potential long range interest to the Air Force involve partially ionized plasmas. Such systems include MPD thrusters, both open and closed cycle MHD power generation, high velocity reentry and thermionic energy conversion. Although the specific configurations, the exact operating conditions, and which of the competing systems will prove to be most useful in the long term remain to be established, it is important at this time to provide a broad fundamental research base in support of development activity. In particular, there are a number of key issues regarding the properties and discharge behavior of partially ionized plasmas and the interaction of discharges with fluid dynamics that need to be understood before the potential and limitations of competing systems can be fully evaluated. In addition, it is important that outstanding young applied scientists be educated in these areas.

Our research on partially ionized plasmas was initiated under grant AFOSR-83-0108 and focused on three major areas:

1. plasma properties,
2. discharge effects: plasma electrode interaction,
3. interaction of discharges and fluid dynamics.

Extensive reports on areas (2) and (3) were given in the previous Annual Scientific Reports. Research this year has emphasized area (1), as does this report.

Progress during the past year on plasma properties is described in the following two sections. Publications and presentations resulting from this work are cited in Section 4 and Section 5 lists the personnel who have contributed to this report.

2-0 MEASUREMENTS OF THE VOLUMETRIC RADIATIVE SOURCE STRENGTH OF AN AIR PLASMA BETWEEN 5000 AND 7500 K

1. Summary

The volumetric radiative source strength of an atmospheric pressure air plasma has been measured between 5000 and 7500 K in a 50 kW inductively coupled plasma torch. The radiation source strength and the temperature profiles, across the axisymmetric 5 cm diameter plasma, have been determined independently and combined. Local thermodynamic equilibrium (LTE) temperatures (based on the absolute intensity of five atomic oxygen and nitrogen lines), Boltzmann temperatures (based on the relative intensity of two oxygen lines), and rotational temperatures from the relative intensity of N_2^+ rotational lines, have been measured. All these temperatures agree within experimental uncertainty. In addition, electron number densities, determined from the width of the $H\beta$ line, are close to equilibrium predictions. Since the foregoing measurements support the assumption of approximate LTE in the plasma, the radiation source strength measurements may be compared with theoretical predictions. Good agreement is obtained with the latest version of the NEQAIR code, but earlier models overestimate the radiation by up to a factor three. The discrepancies may be attributed to inaccurate spectroscopic data and partition functions in the different models.

2. Nomenclature

A_{ji} Einstein emission coefficient (s^{-1}).
 g_j Degeneracy of the j^{th} excited level.
 I_{ji} Total line intensity ($W/cm^3/sr$).
 n_j Number density of j^{th} level.
 P Pressure.
 Q_{el} Electronic partition function.
 S_R Volumetric radiative source strength (W/cm^3sr).
 T_B Boltzmann temperature.
 T_{LTE} Local thermodynamic equilibrium temperature.
 χ_s Mole fraction of species s (oxygen or nitrogen).
 ϵ_{ij} Energy difference between the levels i and j .
 λ Wavelength.

3. Introduction

To understand and model high temperature flows for re-entry, plasma processing or other applications, accurate estimates of the volumetric radiative source strength, or local emissivity, are of importance. In the present paper, we report measurements of several plasma parameters including LTE, Boltzmann and rotational temperatures, electron number density and radiation source strength between 5000 and 7500 K. As will be discussed in Section 5, the temperature and electron number density measurements show that the plasma studied here is close to LTE.

We are only aware of source strength measurements¹⁻⁵ above 9000 K. These were made either in shock tubes (Page¹, Nerem²) or in stabilized arc discharges (Schreiber,³ Ogurtsova,⁴ Devoto⁵). The emitted radiation was recorded by means of thermopiles and calibrated with tungsten ribbon lamps. Temperatures were determined under the assumption of LTE from the absolute intensity of atomic oxygen and nitrogen lines. The spectral range covered generally extended from 0.2 μ m to several μ m. In addition, Schreiber³ extended his measurements to the UV out to 0.05 μ m using an energy balance method incorporating a Hall probe.

In the early 1960s, space programs prompted the development of theoretical models for high-temperature air radiation.⁶⁻⁸ More recently, Space Shuttle re-entry modeling and the Mars Mission sparked new interest in such calculations.⁹ While Kivel,⁶ Meyerott,⁷ and Breene⁸'s models are for air plasmas in local thermodynamic equilibrium, the NEQAIR code, developed

by Park,⁹ can also account for thermal non-equilibrium by incorporating translational, rotational, vibrational and electronic temperatures. For air in LTE, significant differences exist between the results of these four models. These discrepancies are attributable to differences in the methods of calculation and in the radiative transition probabilities. A comparison with the present radiation source strength measurements is presented in Section 6.

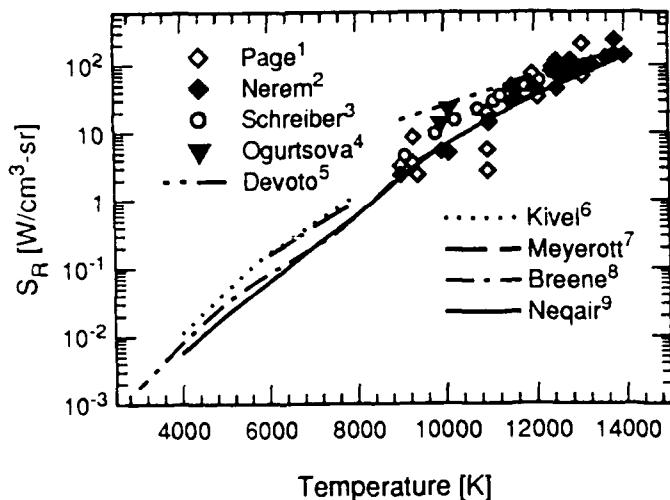


Figure 1. Air source strength

4. Experimental facility

The experiments presented here were conducted with a nominally 50 kW TAFA model 66 RF induction plasma torch, powered by a LEPEL model T-50 power supply. The vertical 5-coil

torch has a 7.5 cm inner diameter and an inner length of 26.5 cm measured between the gas injection plates and the 5 cm diameter exit nozzle, which is 6 cm above the upper coil. All measurements were made 1 cm downstream of the nozzle exit.

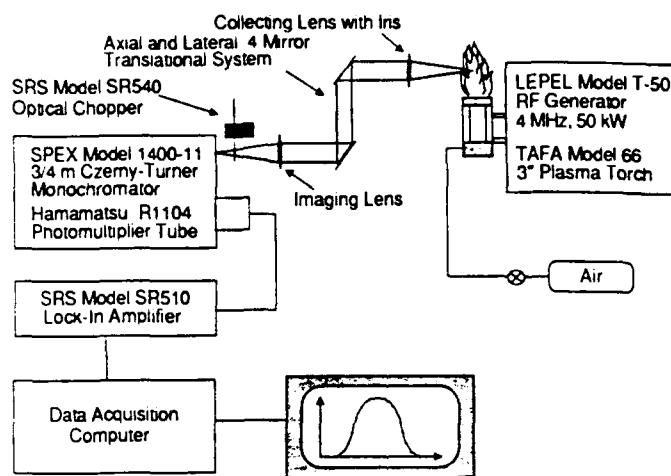


Fig.2. Experimental set-up for emission measurements

tungsten strip lamp, with a calibration traceable to NBS standards. The brightness temperature was measured with an optical pyrometer. The optical arrangement permitted lateral scanning of

Plasma line intensities (Fig.2) were measured using a SPEX model 1400-11 3/4 meter scanning monochromator fitted with a Hamamatsu model R1104 photomultiplier tube. Absolute intensity calibrations were obtained by means of a

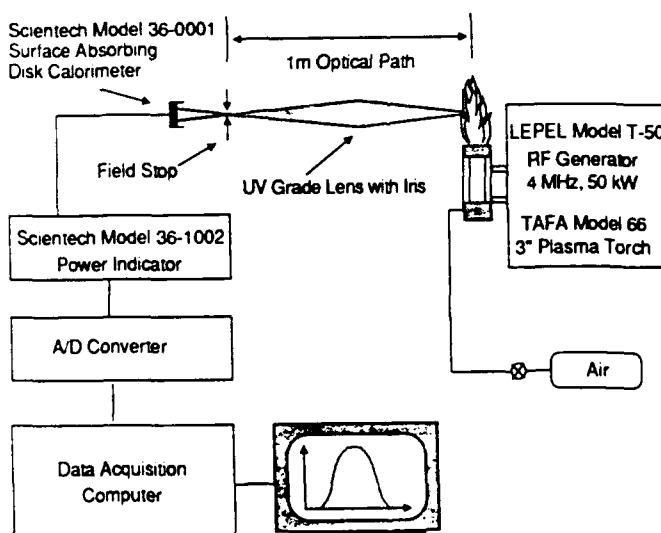


Fig. 3. Experimental set-up for radiation source strength

Total radiation measurements (Fig.3) were made using a self-calibrating Scientech model 36-0001 disc calorimeter, and a mirrorless traversing system including a UV grade quartz lens.

5. Measurements

5.1. Temperature measurements

For a plasma at atmospheric pressure the assumption of local thermodynamic equilibrium is often assumed to be satisfied. However, for purposes of verification, LTE, Boltzmann and rotational temperatures have been determined. In addition, we also measured electron number densities.

5.1.a. LTE temperature

We measured the total intensity from atomic oxygen lines at 777.3 and 615.7 nm, and from a triplet of atomic nitrogen lines at 742.3, 744.2 and 746.8 nm. After subtraction of the continuum signal and calibration, the data were Abel-inverted. The absolute line intensity temperatures, T_{LTE} , were calculated from the Maxwell- Boltzmann relation

$$\frac{n_j}{g_j} = \frac{\chi_s P}{kT_{LTE}} \frac{1}{Q_{el}} \exp\left(-\frac{\epsilon_j}{kT_{LTE}}\right), \quad (1)$$

where n_j is related to the measured line emission coefficient I_{ji} by

$$n_j = \frac{4\pi}{hc} \frac{I_{ji} \lambda_{ji}}{A_{ji}}, \quad (2)$$

and where χ_s stands for the mole fraction of O or N in air at chemical equilibrium. The quantity $\chi_s P/kT$ has been substituted in Eq. (1) for the atomic density. An iterative calculation eventually provides T_{LTE} . The uncertainty is typically 2% over most of the plasma extent. At the edges it increases to about 6% for the 777.3nm O line (most intense line) and 10% for other lines.

5.1.b. Boltzmann temperature

For lines of the same atom with sufficient upper state energy separation (2eV for the two aforementioned oxygen lines), one can infer a temperature independently of the ground state population, considering only that the populations of the emitting levels are in a Boltzmann ratio:

$$\frac{n_{j1}}{n_{j2}} = \frac{g_{j1}}{g_{j2}} \exp\left(-\frac{\epsilon_{j1} - \epsilon_{j2}}{kT_B}\right). \quad (3)$$

Combining Eqs. (2) and (3):

$$\frac{I_{j1i1}}{I_{j2i2}} = \frac{g_{j1} A_{j1i1} \lambda_{j2i2}}{g_{j2} A_{j2i2} \lambda_{j1i1}} \exp\left(-\frac{\epsilon_{j1} - \epsilon_{j2}}{kT_B}\right) \quad (4)$$

from which T_B is readily obtained. Since the energy separation between the two levels is relatively small, the results are quite sensitive to the uncertainty on experimental data and on the Einstein spontaneous emission coefficients. The uncertainty in the Boltzmann temperatures is typically 10%, except at outer radii where it is higher.

5.1.c. Rotational temperature

The rotational lines of the $B\ 2\Sigma_g^+ \rightarrow X\ 2\Sigma_u^+$ (0,0) band of N_2^+ were resolved. They yielded, after Abel inversion, a radial rotational temperature distribution.¹⁰ The accuracy of the resulting rotational temperature profile is however rather poor since the uncertainty on lateral measurements is greatly amplified by the Abel inversion. For this reason, only a temperature inferred from the rotational profile measured along a diameter of the plasma has been indicated in Fig.4. This "average" temperature is consistent with LTE.

5.1.d. Interpretation of the temperature results (see Figure 4)

The values of T_{LTE} from different lines at a fixed radial position are typically within 100K. The Boltzmann temperature T_B agrees within experimental uncertainty, and the averaged

rotational temperature is comparable with T_{LTE} and T_B . This supports the assumption of approximate LTE of the plasma in the considered temperature range. Moreover, since the atomic oxygen and nitrogen line intensities depend (although weakly) on the degree of dissociation, the data are consistent with chemical equilibrium as well.

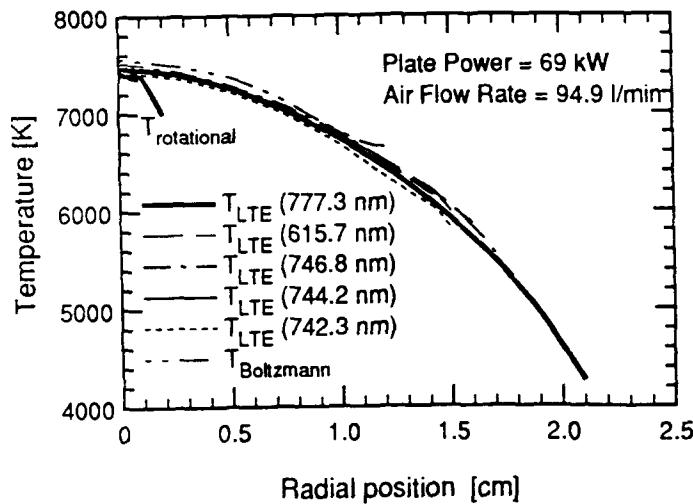


Figure 4. Temperature profiles

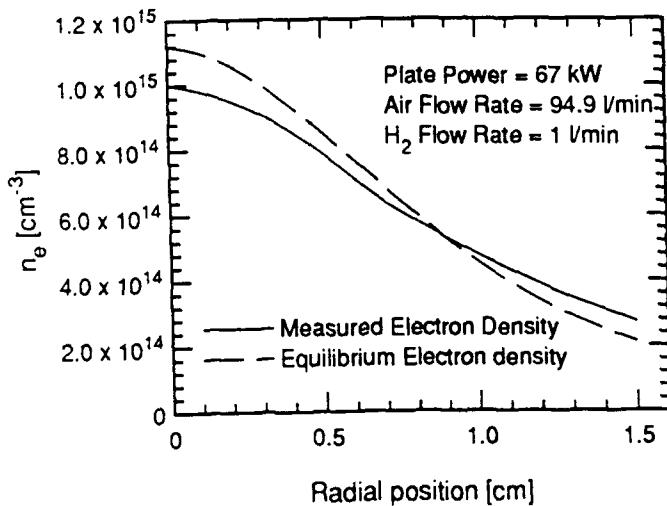


Figure 5. Electron density profile

5.2. Electron number density measurements

Electron number densities have been measured from the width of Abel-inverted profiles of the $H\beta$ line. About 1% of H_2 was mixed with air for that purpose. The LTE temperature measured from the oxygen line at 777.3 nm dropped uniformly over the plasma extent by about 200 K. Based on this temperature, LTE electron number densities were calculated with the Saha equation. The good agreement between these calculations and the measurements

(Fig 5) adds further support to the LTE assumption over most of the plasma.

5.3. Radiation source strength measurements

The radiation source strength as a function of lateral position was measured as described in Section 4. The data were Abel-inverted and reduced to volumetric radiative source strength.

Figure 6 includes a plot of the radiation source strength versus the LTE temperature obtained from the most intense line (OI 777.3 nm), since it allows for the best accuracy.

6. Comparison with theoretical predictions

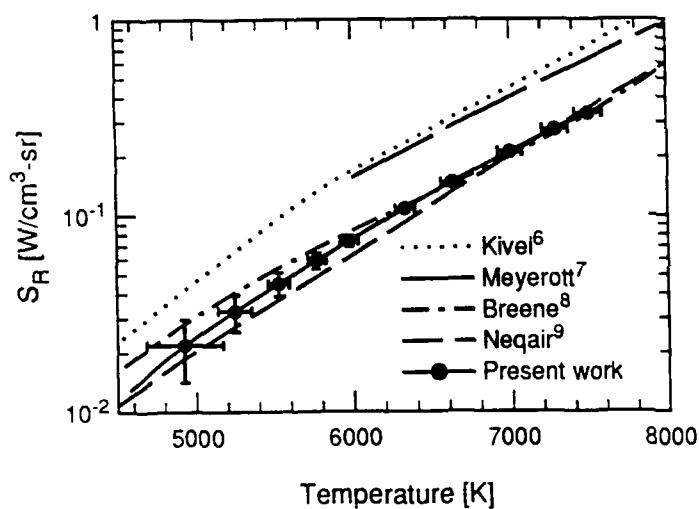


Figure 6. Air source strength

As mentioned earlier, calculations of the radiation source strength have been performed by several authors under the assumption of LTE. The predictions of Kivel⁶ and Meyerott⁷ are higher than our measurements by a factor of two to three. This discrepancy is likely caused by the inaccurate radiative transition probabilities then available. Kivel and Meyerott's transition probabilities are an order of magnitude greater than those used by Breene.⁸ Breene's predictions are much

closer to our measurements, but the agreement might be fortuitous for anomalies in the calculations have been reported by Keck,¹¹ and for the radiative transition probabilities are somewhat different from the currently accepted values.

Modifications have been made to the NEQAIR code⁹ in the form of updated radiative transition probabilities,¹² and of partition functions recalculated¹³ following Lavrov.¹⁴ The resulting predictions are in excellent agreement with our measurements. It should be noted that the radiation from CN has not been included in the NEQAIR calculations but preliminary estimates indicate that it might increase the total radiation by up to 10% at 6000 K.

7. Conclusion

Source strength measurements have been conducted in a plasma found to be close to LTE. This plasma appears as an excellent test ground for high-temperature air radiation modeling. While early models tended to overestimate the radiation, the latest version of the NEQAIR code reproduces accurately the present measurements over a broad temperature range. Spectral measurements are currently under way for purposes of comparison with NEQAIR spectral calculations.

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3-0 ELECTRONIC QUENCHING OF ARGON EXCITED STATES IN A NON-EQUILIBRIUM PLASMA AT ATMOSPHERIC PRESSURE

1. Summary

Emission measurements of temperature and electron density have been made downstream of a 50 kW induction plasma torch at temperatures and electron densities near 7000 K and 10^{20} m^{-3} , respectively. Results indicate that for pure argon plasmas the free and bound-excited electrons are in mutual equilibrium although over-populated with respect to the ground state. The addition of either a hydrogen or nitrogen diluent, however, disturbs this mutual equilibrium because of an exothermic electronic interaction between the diluent's atomic ground state and an argon excited state.

2. Introduction

Most plasma emission diagnostics rely on an assumption of either local thermodynamic equilibrium (LTE) or partial LTE. For an LTE plasma, only one temperature, along with the pressure, is required to specify the thermodynamic state, while for a PLTE plasma another parameter is necessary. A PLTE plasma is characterized by having the bound-excited and free electrons in mutual equilibrium though over or under populated with respect to the ground state. The amount of this over or under population defines the additional parameter required to specify the state in a PLTE plasma. Experimentally, it is often found that although LTE does not exist in many atmospheric argon plasmas, PLTE does hold./1-2/

While pure argon plasmas provide an excellent and relatively simple test condition for plasma diagnostics, plasma mixtures provide a more important condition enabling the study of plasma chemistry. Additionally, mixtures are often used for diagnostic measurements of rotational temperature from molecular transitions or of electron densities from Stark broadened transitions. Accordingly, there is a need to examine the applicability of various emission diagnostics to plasma mixtures.

In this paper, we report absolute and relative atomic line intensities, absolute recombination continuum in both the visible and the ultraviolet, Stark broadening of the hydrogen Balmer lines, and independent calorimetric measurements which demonstrate that the presence of either nitrogen or hydrogen in amounts as small as 0.1% cause departures from PLTE in a recombining atmospheric argon plasma.

3. Experimental Facility

The measurements described here were conducted with a nominally 50 kW TAFA model 66 RF induction plasma torch, powered by a LEPEL model T-50 power supply. The vertical 5-coil torch has a 7.5 cm inner diameter and an inner length of 26.5 cm measured between the gas-injection plate and the 5 cm exit nozzle. The induction coil has a 9 cm diameter and a 7.6 cm length. The present

experiments were conducted at two locations. Spectroscopic measurements reported at the "nozzle exit" were made 1 cm downstream of the actual 5 cm nozzle exit which is itself 7 cm downstream of the last induction coil. Spectroscopic measurements reported at the "test section exit" were made 1 cm downstream of a water cooled quartz test section which has an inner diameter of 5 cm and a length of 17.5 cm above the nozzle exit. The power supply and torch, and the test section cooling water systems, were separately instrumented with thermocouples and flowmeters to independently obtain calorimetric energy balances for comparison with those obtained from spectroscopic measurements.

Plasma emission measurements were made using a SPEX model 1400-11 3/4 meter scanning monochromator fitted with a Hamamatsu model R1104 photomultiplier tube. Absolute intensity calibrations in the visible were obtained by means of a tungsten strip lamp, with a calibration traceable to NBS standards. Temperature measurement of the tungsten strip lamp was made using a Pyro-micro disappearing filament optical pyrometer. Ultraviolet calibration was accomplished using an "equilibrium" condition of the plasma torch.^{3/} A four mirror optical arrangement permitted lateral and axial scanning of the plasma. Data sets acquired using a Stanford Research Systems model SR510 lock-in amplifier were transferred and stored on a laboratory computer for processing. The lateral traverses of emission were transformed to radial variations within the plasma using an Abel inversion technique.

4. Experimental Methods

If, as asserted, neither LTE nor PLTE prevails in our plasma mixtures, the experimental diagnostics which are implemented must directly measure desired parameters independent of these equilibrium assumptions. Absolute atomic line emission measurements lead directly to the population $n_{j,m}$ of a particular species m's excited state through the following relation:

$$n_{j,m} = \frac{4\pi I_{ji}\lambda_{ji}}{hcA_{ji}} \quad (1)$$

where I_{ji} is the emission coefficient, λ_{ji} is the transition's wavelength, h is Planck's constant, c is the speed of light, and A_{ji} is the Einstein transition probability. This measurement is independent of LTE or PLTE, requiring only that the emission is optically thin.

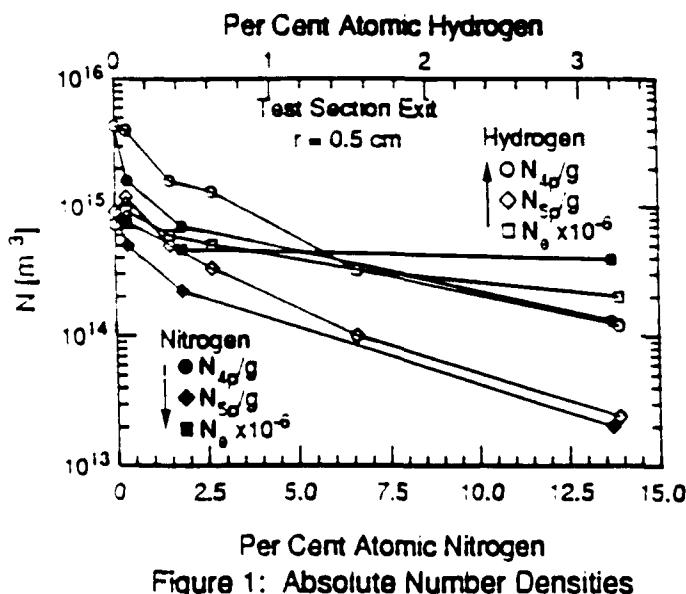
Absolute emission measurements of recombination continuum allow one to evaluate both absolute electron number densities as well as electron kinetic temperatures which are also both independent of LTE or PLTE.^{4/} In general, the recombination emission depends on the electron number density, n_e , the ion number density, n_i , the electron temperature, T_e , the wavelength, λ , and the gas composition. Radiative recombination, the inverse process of photoionization, is symbolically represented as follows:



The energy of the emitted photon, $h\nu$, is the sum of the energy between the ionization limit and the level to which the electron recombines, $\epsilon_j\lambda$, and the kinetic translational energy of the recombining electron, ϵ_{tr} . It is this dependence on the electron translational energy that allows the determination of the electron temperature if the electrons have a Maxwellian velocity distribution. The needed cross-section information describing this recombination is contained in the so-called Biberman factor.^{/5/} For this research, all values for this factor were taken from Hofsaess.^{/6/} At wavelengths above 400 nm, the dependence on T_e is very weak and one can measure n_e for singly ionized plasmas such as ours where $n_i = n_e$. We chose to use 428.5 nm for our measurement. Our inferred n_e was also compared to that obtained from centerline corrected^{/7/} Stark widths of the $H\beta$ line, and agreement to 10% was found. Alternatively, with n_e one can make another emission measurement at a wavelength below 400 nm where the dependence on T_e becomes strong enough to measure. We chose 270 nm to yield T_e with an uncertainty of 6%. In general, this method provides T_e but not the gas temperature, T_g . However, for plasma conditions such as ours where there are minimal electromagnetic fields present, moderate radial temperature gradients, and minimal radiation escape, the electron energy equation predicts a one kinetic temperature plasma such that T_g equals T_e .

5. Results and Discussion

Emission measurements were made at both the nozzle and test section exit for a pure argon plasma and then for an argon plasma with varying amounts of either nitrogen or hydrogen added.



The pure argon plasma has been characterized as an LTE plasma within about 1 cm of the radial center at the nozzle exit and as a PLTE plasma within about 1.6 cm of the radial center at the test section exit.^{/2/} The diluent is added to this established experimental condition. In all cases, emission coefficients were measured at 715 nm, 430 nm, 428.5 nm, and 270 nm to yield argon n_{4p} , argon n_{5p} , total n_e , and T_e , respectively. Figure 1 shows n_{4p} , n_{5p} , and n_e for all test conditions at the test section exit. We clearly see a drop in all

number densities with the addition of diluent, although the cause is not apparent from this figure alone. Note that this and several other graphs have two abscissas. The solid data correspond to the addition of nitrogen into the argon plasma with the per cent of atomic nitrogen added read on the bottom abscissa. The open data correspond to the addition of hydrogen with the amount read on the top abscissa.

Since the undiluted plasma is in PLTE at the test section exit, the bound-excited and free electrons are in Saha equilibrium at T_e such that T_e determines the ratio of n_j to n_e^2 . One can then evaluate the ratio of n_j to n_e^2 for cases with diluent normalized to the case without diluent to

investigate whether PLTE is maintained.

As Figure 2 shows, this parameter decreases for increasing amounts of diluent. If PLTE still holds, this decrease implies an increase in T_e . However, as will be demonstrated shortly (Figure 3), T_e actually decreases with increased amounts of diluent. We therefore conclude that the addition of diluent causes the plasma to depart from PLTE.

To quantify this departure from PLTE, T_e is required. Although in theory the ultraviolet recombination measurement can

directly measure T_e , in practice its uncertainties - especially near the radial center and edges of the plasma - preclude its use as a sufficiently precise technique. However, because the pure argon plasma has been shown to be in PLTE at the test section exit, both the Boltzmann temperature inferred from relative argon excited state populations and the line to continuum temperature inferred

from an excited state Saha equation equal the electron temperature. These two temperature profiles agree well out to about 1.6 cm with both $T_e/3$ and with a temperature profile generated from a fluid dynamics code⁸ constrained to agree at the radial center. Further, the code's output was perturbed by less than 2% when the thermodynamic properties were adjusted to account for the presence of the diluent. Consequently, the computer generated shape is taken as the electron temperature shape for all cases with its

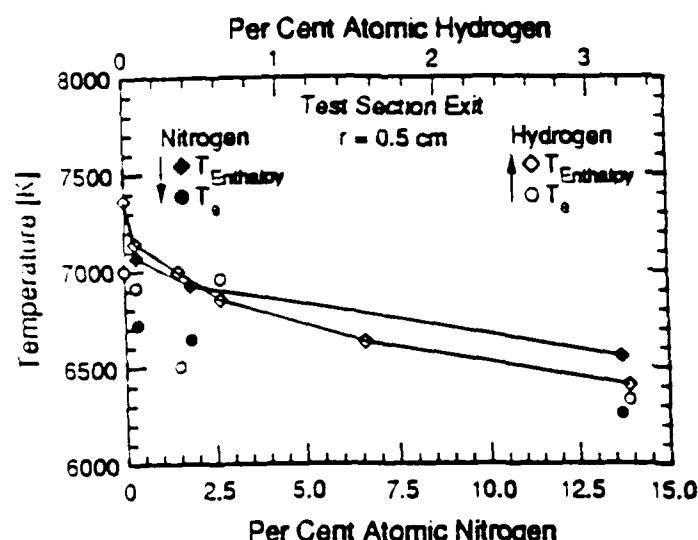


Figure 2: PLTE Comparison Parameter

absolute magnitude known for pure argon. To evaluate the magnitude of this profile for cases with diluent, a calorimetric energy balance was utilized.

The enthalpy flux was monitored at both the nozzle and test section exit. For all experimental cases, the measured sensible fluxes were kept within 3% of each other at the nozzle exit through adjustment of the plate input power. That is, the input power was adjusted so that the nozzle exit

temperatures remained nearly the same in the presence of the diluent. Because the 8400 K temperature at the nozzle exit is sufficient to completely dissociate the diluents, the corresponding total enthalpy fluxes for the cases with hydrogen and particularly nitrogen - because of nitrogen's larger dissociation energy - are larger than that for pure argon. Since the nozzle exit temperatures are then all taken to be the same, one can infer T_e at the test section exit for each case with diluent by

comparing its measured enthalpy drop across the test section including radiative losses/2/ to the enthalpy drop for the pure argon case. For example, at the test section exit, we calorimetrically measure a sensible enthalpy of 10 kW for pure argon. For every additional 1 kW of calorimetric loss measured across the test section resulting from the addition of diluent, then, T_e would drop 10%. This approach assumes that there is negligible recombination of the diluent between the nozzle exit and the test section exit. An equilibrium analysis of the

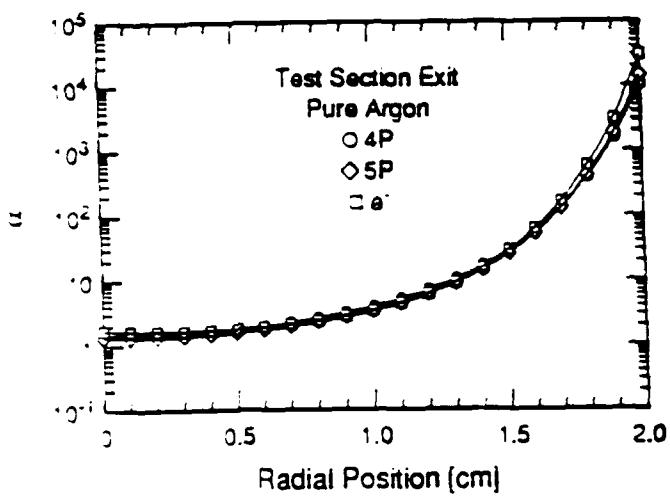


Figure 4: Alpha

various gas compositions at the inferred T_e show that this is valid for all test conditions except for the largest addition of nitrogen. Preliminary modelling of this recombination process with time dependency - CHEMKIN - suggests that nitrogen recombination would lag equilibrium for our conditions. Experimental emission measurements of the N_2^+ 1st negative and N_2 2nd positive band heads also show that compared to equilibrium, the emission is less than expected indicating hindered recombination of atomic nitrogen. Plotted in Figure 3, then, are the resulting test section exit temperatures 0.5 cm from the radial center along with the corresponding ultraviolet T_e . Recalling that T_e is 6% uncertain, generally good agreement is observed.

With T_e , the deviation from LTE and PLTE can be quantified. Under the assumption of LTE for our atmospheric pressure plasma, equilibrium argon excited state populations, n_j^* , and equilibrium electron number densities, n_e^* , can be calculated. A useful non-dimensional parameter which then reflects the deviation from LTE is alpha, defined by the following:

$$\alpha_j = \frac{n_j}{n_j^*} \quad \alpha_e = \left(\frac{n_e}{n_e^*} \right)^2 \quad (3)$$

Plotted in figure 4 is alpha for the pure argon case at the test section exit. We see that the plasma deviates by over an order of magnitude from LTE for radial positions greater than about 1.3 cm, but that the agreement among all the alphas implies PLTE. This is one of the primary tests of PLTE. Figure 5 plots alpha for two representative cases with diluent, also at the test section exit. Here we see more evidence of non-PLTE. For both nitrogen and hydrogen, the alphas differ by a factor of

between five and ten demonstrating the absence of PLTE. We also see that the 4p level is closest to LTE and the free electrons are furthest from LTE suggesting the diluent's effect is upon argon's lower energy levels.

To better understand this phenomena, we need to examine first why the pure argon case deviates from LTE. Recall that we take our emission measurements nearly 30 cm downstream of the center

of the coil region where the power is deposited. This creates a recombining plasma as it loses energy primarily through conduction and radiation. Because the electronic structure of argon allows excited states to collisionally or radiatively return to ground from states that are all over 11.5 eV in energy above the ground state, collisional de-excitation by an electron or argon atom or ion is slow. Radiative de-excitation to the ground state is heavily trapped which further hinders the recombination process. Diffusion of

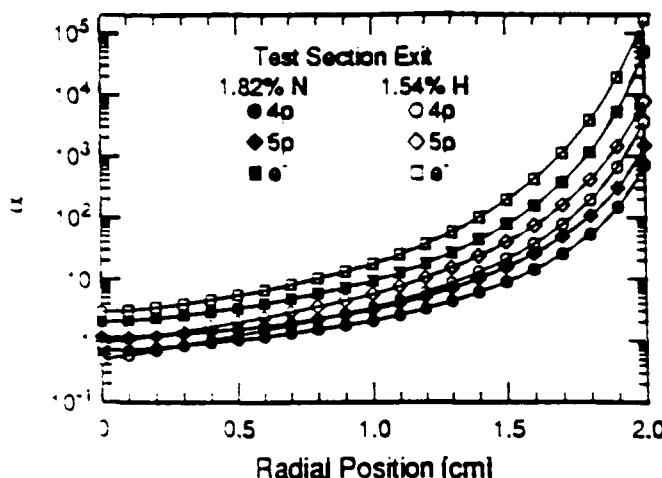
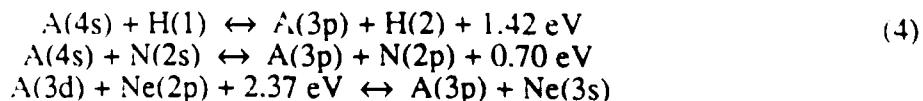


Figure 5: Alpha

excited states and free electrons from the hotter core to the colder plasma edges also contributes to the deviation from LTE creating the largest deviations near the plasma edges. According to argon collisional-radiative models,/9-10/ if n_e is sufficient, PLTE with the bound-excited levels - especially the higher energy states - is expected, and this PLTE is indeed observed down to the lowest level accessible through emission, the 4p. Since electrons recombine predominantly with argon ions to form an excited state rather than a ground state atom, for the recombining pure argon plasma, deviations from LTE are controlled by the finite recombination rates of the argon excited states to ground.

With the introduction of either atomic nitrogen or hydrogen, however, argon excited states have additional collision partners for transitions to ground. This type of de-excitation, or quenching, caused by molecular diluents interacting with argon's 4s level is already well documented./11-13/ These previous experiments suggest that the transitions in the molecular diluents which quench best are ones with an energy separation that is less than that for the argon transition to ground. These types of transitions result in a relatively fast exothermic two-body reaction in contrast to a slower endothermic one if the diluent's transition has an energy separation larger than argon's. Both atomic nitrogen and hydrogen have at least two such exothermic transitions. Neon, in contrast, has only endothermic quenching transitions; therefore an experiment with the addition of neon as the diluent will serve as an experimental check./11/ The following reactions are representative examples:



The quenching of argon excited states by the addition of certain diluents now explains the observed reduction in α_{4p} and α_{5p} as compared to the pure argon case (Figures 4 and 5). To understand the departure from PLTE, finite electron recombination rates and finite electron collision rates must be considered. The differences between α_e and both α_{4p} and α_{5p} suggest that the electron recombination rate is not fast enough to follow the relatively quick quenching of argon excited states. The differences between α_{4p} and α_{5p} suggest that the electron collision rate with the

argon excited states is also not fast enough - again relative to the diluent's quenching rate - to maintain even a PLTE among just the excited states. This model implies a competition between electron collisions with argon excited states attempting to maintain PLTE with the over-populated electrons, and diluent collisions attempting to quench these excited states in the direction of approximate equilibrium with the ground state. For analytical purposes, we define $n_{j*}e$ to be a given argon excited state's population in equilibrium with the

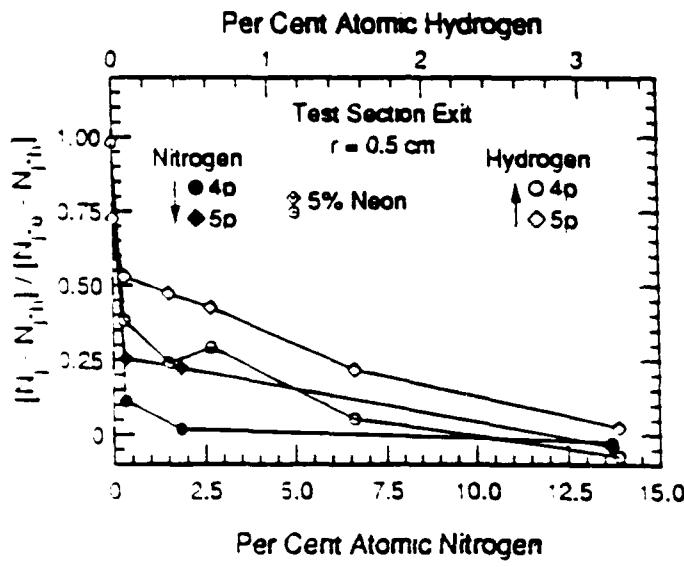


Figure 6: Quenching Parameter

free electrons at T_e and $n_{j*}h$ to be a given argon excited state's population in equilibrium with the ground state at T_e . Plotted in Figure 6 is a parameter which combines these defined populations with those experimentally determined to quantify the degree of quenching. This parameter, however, better describes deviations from PLTE and relative degree of quenching than it describes absolute quenching. Alpha is best for determining whether equilibrium with the ground state exists. In any case, Figure 6 clearly shows that the degree of quenching at the test section exit is increased for increasing amounts of diluent, and that even 0.07% atomic hydrogen causes deviations from PLTE. We also see that as expected the 4p level which is closer in energy to either of the possibly quenched argon levels is more strongly depopulated than is the 5p level. Also plotted is one data pair for 5% neon which shows minimal quenching thereby supporting the idea that the diluent should have a exothermic transition with respect to the relevant transition in argon.

6. Conclusion

Experimental measurements of argon excited state densities and electron number densities indicate that a PLTE exists for a recombining pure argon plasma such that the free and bound-excited electrons are in equilibrium though over-populated with respect to the ground state. The addition of either nitrogen or hydrogen, however, in amounts as small as 0.1% cause deviations from this PLTE. Both diluents have an exothermic transition with an excited state in argon. Experiments with neon which has an endothermic coupling, in contrast, demonstrated negligible quenching.

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4.0 PUBLICATIONS AND PRESENTATIONS

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5.0 PERSONNEL

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